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(54) **A process for the production of paper**

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Procédé de production de papier

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**EP-A- 0 223 223** **EP-A- 0 235 893**  
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• **"Aluminium Based Micro particulate Retention  
aid systems" by Lindström T et al, Nordic Pulp  
and Paper Res. Journal, No 2, 1989, pp. 99-103**

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**Description**

[0001] The present invention relates to a process for the production of paper and, more particularly, to a process in which a low molecular weight cationic polymer, a high molecular weight charged polymer and anionic inorganic particles are added to a papermaking stock. The process provides improved drainage and retention.

**Background**

[0002] It is known in the art to use systems of drainage and retention aids comprising high molecular weight (hereafter HMW) charged polymers and anionic inorganic particles, e.g. bentonite and silica based particles. These additives are introduced into the stock in order to facilitate drainage and increase adsorption of fine particles onto the cellulose fibres so that they are retained with the fibres. However, the efficiency of drainage and retention aids usually is deteriorated in stocks which have a high cationic demand due to the presence of interfering anionic substances. In the art, such substances are commonly referred to as anionic trash. The level of anionic trash usually is high in stocks based on recycled fibres and mechanically derived pulps. To counter the deteriorated performance of additives observed in such stocks, it is known to use low molecular weight (hereafter LMW) cationic polymers as anionic trash catchers which are initially added to the stock in order to neutralize the anionic trash and reduce the cationic demand, thereby enhancing the efficiency of drainage and retention aids subsequently added.

[0003] EP-A-0335575 discloses a process for the production of paper which comprises a preliminary polymer inclusion stage in which a LMW cationic polymer is added to a cellulosic suspension followed by addition of a main polymer selected from cationic starch or HMW cationic polymer and then an inorganic material selected from bentonite or colloidal silica.

[0004] EP-A-0308752 relates to a method for making paper which comprises the steps of adding to paper furnish a LMW cationic organic polymer and then colloidal silica and a HMW charged acrylamide copolymer having a molecular weight of at least 500,000.

**The Invention**

[0005] According to the present invention it has been found that very good drainage and/or retention can be obtained with additives comprising LMW cationic polymer, HMW cationic and/or amphoteric polymer and anionic inorganic particles when the LMW cationic polymer and HMW cationic and/or amphoteric polymer are simultaneously added to the stock, in particular when using the LMW polymer and HMW polymer in the form of a mixture. This discovery is contrary to prior art techniques which emphasize the initial addition of LMW cationic polymers for obtaining adequate performance with subsequently added drainage and retention aids comprising HMW charged polymers and anionic inorganic particles. More specifically, the present invention relates to a process for the production of paper from a suspension of cellulose containing fibres, and optional fillers, which comprises adding to the suspension a low molecular weight cationic organic polymer, a high molecular weight cationic and/or amphoteric polymer and anionic inorganic particles, forming and draining the suspension on a wire, wherein the low molecular weight polymer has a molecular weight below 700,000; the high molecular weight polymer has a molecular weight above 1,000,000; and said polymers are simultaneously added to the suspension with substantially no time difference and essentially at the same position. The invention thus relates to a process as further defined in the claims.

[0006] The process according to the present invention results in improved drainage and/or retention compared to processes in which HMW cationic or amphoteric polymers are used as a sole polymer additive in conjunction with anionic inorganic particles. Furthermore, the present process results in improved drainage and/or retention compared to processes comprising pre-dosing LMW cationic polymer prior to adding HMW cationic and/or amphoteric polymers and anionic inorganic particles. Hereby the present invention makes it possible to increase the speed of the paper machine and to use lower dosages of additives to give the same drainage and/or retention effect, which lead to an improved papermaking process and economic benefits.

[0007] The polymers simultaneously added to the stock according to the invention comprise at least one high molecular weight charged polymer that functions as a drainage and/or retention aid. The HMW polymer can be selected from cationic polymers, amphoteric polymers or mixtures thereof. The use of such polymers as drainage and/or retention aids is known in the art. Preferred HMW polymers are water-soluble. Suitably at least one HMW cationic organic polymer is used. Generally, the cationicity of the HMW polymers can be within the range of from 1 to 100 mole%, suitably from 1 to 80 mole% and preferably from 1 to 60 mole%. The term "cationicity", as used herein, refers to the amount of cationic mer units present in the polymer. The charge density of the HMW polymer can be from 200 to 7,000  $\mu\text{eq/g}$  of dry polymer. The HMW polymer can be derived from natural or synthetic sources, and it can be linear or branched. Examples of suitable polymers include cationic and amphoteric starches, guar gums, acrylamide-based and N-vinylamide-based polymers, polymers based on diallyldimethylammonium chloride and cationic polyethylene imines,

polyamines and polyamideamines. Cationic starches, guar gums and acrylamide-based polymers are preferred HMW polymers. The molecular weight of the HMW polymer is above 1,000,000 and preferably above 2,000,000. The upper limit is not critical; it can be about 50,000,000, usually 30,000,000 and suitably 25,000,000. However, the molecular weight of polymers derived from natural sources may be higher.

5 **[0008]** The polymers simultaneously added to the stock according to the invention further comprises at least one low molecular weight cationic organic polymer. Preferred polymers include water-soluble, highly charged LMW polymers which can have a cationicity of from 10 to 100 mole%, suitably from 20 to 100 mole% and preferably from 50 to 100 mole%. The charge density of the LMW polymer can be above 1,000  $\mu\text{eq/g}$ , suitably above 2,000  $\mu\text{eq/g}$  and preferably within the range of from 3,000 to 15,000  $\mu\text{eq/g}$  of dry polymer. It is preferred that the LMW polymer has a higher cationicity and/or higher cationic charge density than the HMW polymer. Examples of suitable LMW cationic polymers include modified starches, e.g. degraded starch, polyamines, polyethylene imine, polyamideamine/epichlorohydrin, dialkylamine/epichlorohydrin, homo- and copolymers based on monomers selected from diallyldimethylammonium chloride, vinyl amines, (meth)acrylamides and (meth)acrylates. Preferred LMW cationic polymers include polyamines, polyethylene imines, epichlorohydrin-based polymers and diallyldimethylammonium chloride-based polymers. The cationic monomers can be acid addition salts and/or quaternary ammonium salts. Examples of suitable (meth)acrylamides and (meth)acrylates include dialkylaminoalkyl (meth)acrylamides and dialkylaminoalkyl (meth)acrylates, preferably their quaternary ammonium salts. The molecular weight of the LMW cationic polymer may depend on the type of polymer and its charge density. The molecular weight is below 700,000 and preferably below 500,000. The lower limit is usually 2,000 and preferably about 5,000.

20 **[0009]** The weight ratio of HMW polymer to LMW polymer added to the stock according to the invention can be varied over a broad range and it can be within the range from 30:1 to 1:20, usually from 20:1 to 1:20, suitably from 9:1 to 1:3, preferably from 7:1 to 1:2 and most preferably from 5:1 to 1:1.

25 **[0010]** The simultaneous addition to the stock of the HMW and LMW polymers according to the invention can be conducted at any position in the paper machine or stock preparation department. Hereby is meant that the polymers are added to the stock with substantially no time difference and essentially at the same position in the stock preparation department or paper machine prior to draining the stock on the wire. This means that the polymers can be added in the form of a mixture as well as separately, e.g. by adding one polymer during the addition of the other.

30 **[0011]** According to a preferred embodiment of the invention, the LMW cationic polymer in admixture with the HMW cationic and/or amphoteric polymer are added to the stock. The use of a polymer mixture and anionic inorganic particles according to the invention provides considerable improvements over prior art processes, in particular improved retention performance in stocks having a high cationic demand. The addition of a polymer mixture containing both LMW polymer and HMW polymer is further advantageous from an operational viewpoint since the number of polymer additions required can be reduced. Hereby it is possible to dispense with storage tanks, dosing equipment, control devices, etc., otherwise needed for polymer dosage, leading to a simplified papermaking process.

35 **[0012]** The polymer mixture of this embodiment can be prepared at any time prior to incorporating it into the stock, for example by mixing the polymers which may be in any state of aggregation, e.g. solids, solutions, emulsions, dispersions and mixtures thereof. When being added to the stock, the polymer mixture suitably is in a liquid form, e.g. in the form of an aqueous solution or dispersion.

40 **[0013]** In a preferred embodiment, use is made of a freshly prepared mixture of HMW polymer and LMW polymer, as defined above. Such a pre-mix can be formed by bringing an aqueous stream of HMW polymer into contact with an aqueous stream of LMW polymer and then introducing the resulting stream into the suspension. If desired, the streams can be mixed by means of any mixing device having at least two inlets into which separate streams of the polymers to be mixed are supplied and having at least one outlet through which the resulting mixture is passed and subsequently introduced into the stock.

45 **[0014]** The present invention further relates to a mixture of water-soluble polymers in the form of an aqueous dispersion containing at least one high molecular weight cationic or amphoteric acrylamide-based polymer having a molecular weight above 1,000,000, at least one low molecular weight cationic organic polymer having a molecular weight below 700,000 and at least one water-soluble inorganic salt, wherein the weight ratio of said high molecular weight polymer to said low molecular weight polymer is within the range of from 9:1 to 1:2 and the dispersion comprises particles of high molecular weight cationic or amphoteric acrylamide-based polymer. The polymer mixture provides improved drainage and/or retention when used in combination with anionic inorganic particles. In the polymer mixture according to the invention, the HMW polymer is a cationic and/or amphoteric acrylamide-based polymer, preferably a cationic acrylamide-based polymer. The HMW polymer can have a cationicity ranging from 1 to 100 mole%, suitably from 1 to 80 mole% and preferably from 1 to 60 mole%, and it can have a charge density within the range of from 200 to 7,000  $\mu\text{eq/g}$  of dry polymer. The molecular weight of the HMW polymer is above 1,000,000 and preferably above 2,000,000. The upper limit is not critical; it can be about 50,000,000, usually 30,000,000 and suitably 25,000,000. The LMW cationic polymer preferably is a homo- or copolymer based on monomers selected from diallyldimethylammonium chloride, vinylamines, (meth)acrylamides, e.g. dialkylaminoalkyl (meth)acrylamides, (meth)acrylates, e.g. dialkylami-

noalkyl (meth)acrylates, or mixtures thereof. The cationic monomers can be acid addition salts and/or quaternary ammonium salts, preferably quaternary ammonium salts. The LMW cationic polymer can have a cationicity within the range of from 10 to 100 mole%, suitably from 20 to 100 mole% and preferably from 50 to 100 mole%, and it can have a charge density above 1,000  $\mu\text{eq/g}$ , suitably above 2,000  $\mu\text{eq/g}$  and preferably within the range of from 3,000 to 15,000  $\mu\text{eq/g}$  of dry polymer. It is preferred that the LMW polymer has a higher cationicity and/or higher cationic charge density than the HMW polymer. The weight ratio of HMW polymer to LMW polymer is within the range of from 9:1, suitably from 7:1 and preferably from 5:1, to 1:2, suitably to 1:1 and preferably to 2:1. The aqueous dispersion of polymers can have a high dry polymer content, e.g. ranging from 5 to 75% by weight and suitably from 10 to 60% by weight.

**[0015]** In the polymer mixture according to the invention, it is preferred that the inorganic salt is an inorganic salt producing an aqueous phase in which the HMW polymer is insoluble. Examples of suitable salts include sodium sulfate, ammonium sulfate, magnesium sulfate, aluminium sulfate, sodium chloride, sodium dihydrogenphosphate, diammonium hydrogenphosphate and dipotassium hydrogenphosphate. Generally, polyvalent anion salts are preferred, e.g. the sulfates. The amount of water-soluble salt present in the polymer dispersions can be at least 2% by weight, based on the dispersion, and suitably the amount is within the range of from about 5% up to the limit of solubility of the salt, e.g. up to 50%.

**[0016]** The subject polymer mixture can be obtained by polymerization of water-soluble monomers intended for formation of the HMW polymer in an aqueous phase containing the LMW cationic polymer and the inorganic salt. Examples of suitable monomers include (meth)acrylamide, (meth)acrylamide-based monomers, e.g. dialkylaminoalkyl (meth)acrylamides, acid addition salts and quaternary ammonium salts thereof, (meth)acrylate-based monomers, e.g. dialkylaminoalkyl (meth)acrylates, acid addition salts and quaternary ammonium salts thereof, diallyldialkylammonium halides, e.g. diallyldimethylammonium chloride, and the like. The HMW polymer formed is precipitated in the aqueous phase due to the presence of the inorganic salt and the fine particles of HMW polymer so obtained are dispersed and stabilized in the aqueous phase by means of the LMW polymer. Generally, the polymerization of monomers in the presence of salt and polymeric dispersing agents is known in the art, for example from EP-A-0183466 and EP-A-0525751, and the present polymer mixture can be prepared according to the methods disclosed therein except that other polymers and/or weight ratios are used to produce the polymer mixture of the present invention.

**[0017]** The amount of polymers added to the stock according to the process of the present invention can be varied over a broad range depending on, among other things, the type of polymers used and if the polymers are utilized for further purposes. In addition to providing drainage and/or retention, the polymers may impart wet-strength and dry-strength to the cellulosic web or sheet produced. Examples of wet-strength improving polymer combinations include HMW cationic starch and cationic acrylamide-based polymer in combination with polyamideamine/epichlorohydrin. Usually, the total amount of polymers added is within the range of from 0.01 to 30 kg/ton, calculated as dry polymers on dry fibres and optional fillers. When using synthetic HMW polymers, e.g. cationic polyacrylamides, the total amount of polymers usually is at least 0.01 kg/ton, suitably from 0.02 to 15 kg/ton and preferably from 0.05 to 8 kg/ton. When using HMW polymers derived from natural sources such as those based on carbohydrates, e.g. cationic starch and cationic guar gum, the total amount of polymers usually is at least 0.05 kg/ton, calculated as dry polymers on dry fibres and optional fillers, suitably from 0.1 to 30 kg/ton and preferably from 1 to 20 kg/ton.

**[0018]** Anionic inorganic particles that can be used according to the invention include silica based particles, clays of the smectite type and titanyl sulphate sols. It is preferred that the particles are colloidal, i.e. in the colloidal range of particle size. It is preferred to use silica based particles, i.e. particles based on  $\text{SiO}_2$ , including colloidal silica, colloidal aluminium-modified silica or aluminium silicate, different types of polysilicic acid and mixtures thereof, either alone or in combination with other types of anionic inorganic particles. Suitable silica based particles include those disclosed in US-A-4,388,150, US-A-4,954,220, US-A-4,961,825, US-A-4,980,025, US-A-5,127,994, US-A-5,176,891, US-A-5,368,833, US-A-5,447,604, EP-A-0656872, and WO-A-95/23021.

**[0019]** The silica based particles suitably have a particle size below about 50 nm, preferably below about 20 nm and more preferably in the range of from about 1 to about 10 nm. The silica based particles suitably have a specific surface area above 50  $\text{m}^2/\text{g}$ , preferably above 100  $\text{m}^2/\text{g}$ , and suitably up to about 1700  $\text{m}^2/\text{g}$ . The specific surface area can be measured by means of titration with NaOH according to the method described by Sears in Analytical Chemistry 28 (1956):12, 1981-1983.

**[0020]** According to a preferred embodiment of the invention, the silica based particles have a specific surface area within the range of from 50 to 1000  $\text{m}^2/\text{g}$  and suitably from 100 to 950  $\text{m}^2/\text{g}$ . In a particularly preferred embodiment, use is made of a silica sol having an S-value within the range of from 8 to 45%, preferably from 10 to 30%, containing silica particles having a specific surface area within the range of from 750 to 1000  $\text{m}^2/\text{g}$ , preferably from 800 to 950  $\text{m}^2/\text{g}$ , which are surface-modified with aluminium to a degree of from 2 to 25% substitution of silicon atoms, as disclosed in US-A-5,368,833. The S-value can be measured and calculated as described by Iler & Dalton in J. Phys. Chem. 60 (1956), 955-957. The S-value indicates the degree of aggregate or microgel formation and a lower S-value is indicative of a higher degree of aggregation.

[0021] According to another preferred embodiment of the invention, use is made of a polysilicic acid having a high specific surface area, suitably above about 1000 m<sup>2</sup>/g. In the art, polysilicic acid is also referred to as polymeric silicic acid, polysilicic acid microgel and polysilicate microgel, which are all encompassed by the term polysilicic acid. Suitably, the polysilicic acid has a specific surface area within the range of from 1000 to 1700 m<sup>2</sup>/g, preferably from 1050 to 1600 m<sup>2</sup>/g. Polysilicic acids that can be used according to the present invention include those disclosed in US-A-4,388,150, US-A-4,954,220, US-A-5,127,994 and US-A-5,279,807.

[0022] According to another preferred embodiment of the invention, use is made of colloidal aluminium-modified silica or aluminium silicate having a high specific surface area, suitably above about 1000 m<sup>2</sup>/g. In the art, compounds of this type are also referred to as polyaluminosilicates and poly-aluminosilicate microgels, which are both encompassed by the terms colloidal aluminium-modified silica and aluminium silicate used herein. Suitably, the specific surface area is within the range of from 1000 to 1700 m<sup>2</sup>/g, preferably from 1050 to 1600 m<sup>2</sup>/g. Examples of suitable high surface area silica based particles of this type include those disclosed in US-A-4,961,825, US-A-4,980,025, US-A-4,927,498, US-A-5,176,891 and US-A-5,470,435.

[0023] Clays of the smectite type that can be used in the present process are known in the art and include naturally occurring, synthetic and chemically treated materials. Examples of suitable smectite clays include montmorillonite/bentonite, hectorite, beidelite, nontronite and saponite, preferably bentonite and especially such which after swelling preferably has a surface area of from 400 to 800 m<sup>2</sup>/g. Suitable bentonites and hectorites are disclosed in EP 0235893 and EP 0446205, respectively, which are both incorporated herein by reference. Suitable mixtures of silica based particles and smectite clays, preferably natural sodium bentonite, are disclosed in WO-A-94/05595 which is likewise incorporated herein by reference, wherein the weight ratio of silica based particles to clay particles can be in the range of from 20:1 to 1:10, preferably from 6:1 to 1:3. Useful titanyl sulphate sols are for example disclosed in EP-A-0148647.

[0024] The amount of anionic inorganic particles added to the suspension may vary within wide limits depending on; among other things, the type of particles used. The amount usually is at least 0.01 kg/ton and often at least 0.05 kg/ton, calculated as dry particles on dry fibres and optional fillers. The upper limit can be 10 kg/ton and suitably is 5 kg/ton. When using silica based particles, the amount suitably is within the range of from 0.05 to 5 kg/ton, calculated as SiO<sub>2</sub> on dry stock system, and preferably from 0.1 to 2 kg/ton.

[0025] In the present process it is preferred to add the polymers to the stock before the anionic inorganic particles, even if the opposite order of addition may be used. It is further preferred to add the first component, e.g. the polymers, before a shear stage which can be selected for example from pumping, mixing, cleaning, etc., and to add the second component, e.g. the anionic inorganic particles, after that shear stage. The present process further encompasses split additions, e.g. at least two positions for simultaneously adding the polymers, either separately or in admixture, and/or at least two positions for adding anionic inorganic particles, preferably with a shear stage between each addition. The high dewatering and retention effects observed with the additives of the invention can be obtained over a broad stock pH range. The pH can be in the range from about 3 to about 10, suitably above 3.5 and preferably within the range of from 4 to 9.

[0026] Additives which are conventional in papermaking such as, for example, stock sizes based on rosin, ketene dimers or alkenyl succinic anhydrides, dry strength agents, wet strength agents, aluminium compounds, etc., can of course be co-used in the process of the invention. The improved performance observed in the process of the present invention means that further benefits can be obtained, such as for example improved retention of such additives which can lead to improved sizing and strength of the paper. Aluminium compounds can be used to further improve drainage and/or retention in the present process. Examples of suitable aluminium compounds that can be used include alum, aluminates, aluminium chloride, aluminium nitrate and polyaluminium compounds, such as polyaluminium chlorides, polyaluminium sulphates, polyaluminium compounds containing both chloride and sulphate ions and polyaluminium silicate-sulphates. The suspension or stock can also contain mineral fillers of conventional types such as, for example, kaolin, china clay, titanium dioxide, gypsum, talc and natural and synthetic calcium carbonates such as chalk, ground marble and precipitated calcium carbonate.

[0027] The process according to the invention can be used for producing cellulose fibre containing products in sheet or web form such as for example pulp sheets and paper. It is preferred that the present process is used for the production of paper. The term "paper", as used herein, of course include not only paper and the production thereof, but also other sheet or web-like products, such as for example board and paperboard, and the production thereof.

[0028] The process according to the invention can be used in the production of sheet or web-like products from different types of aqueous suspensions containing cellulosic fibres, or stocks, and the suspensions suitably contain at least 25% by weight and preferably at least 50% by weight of such fibres, based on dry substance. The suspensions can be based on fibres from chemical pulp such as sulphate and sulphite pulp, mechanical pulp such as thermomechanical pulp, chemo-thermomechanical pulp, refiner pulp and groundwood pulp, from both hardwood and softwood, and can also be based on recycled fibres from de-inked pulps, and mixtures thereof. It is preferred that at least 10% by weight and preferably at least 20% by weight of the pulp is derived from recycled fibre, de-inked pulp, coated broke or mechanical pulp or any mixture thereof. Such stocks, normally, have a high cationic demand and contains high

levels of anionic trash which may be pulping residues, bleaching residues, de-inking residues, binders, inks, fillers, fines, sizes, dispersing agents and deposit control chemicals.

[0029] The invention is further illustrated in the following Examples which, however, are not intended to limit same. Parts and % relate to parts by weight and % by weight, respectively, unless otherwise stated.

#### Example 1

[0030] In the following tests, drainage performance was evaluated by means of a Dynamic Drainage Analyser (DDA), available from Akribi, Sweden, which measures the time for draining a set volume of stock through a wire when removing a plug and applying a vacuum to that side of the wire opposite to the side on which the stock is present.

[0031] The furnish contained 54% of pulp based on a 60:40 mixture of bleached birch:pine sulphate refined to 200° CSF, 23% of ground marble and 23% of coated broke (magazine paper) having an ash content of 30%. Stock volume was 800 ml, consistency 0.3% and pH about 7. The stock was stirred in a baffled jar at a speed of 1500 rpm throughout the test and chemical additions to the stock were conducted as follows: i) adding either HMW polymer used for comparison purposes or polymers according to the invention followed by stirring for 30 seconds, ii) adding anionic inorganic particles followed by stirring for 15 seconds, iii) draining the stock while automatically recording the drainage time.

[0032] A polymer mixture, herein designated M1, in the form of an aqueous dispersion of a HMW cationic polyacrylamide and a LMW cationic polyacrylate was used in the process of the invention. The polymer mixture was prepared by polymerization of acrylamide (90 mole%) and methacryloyloxyethyltrimethylbenzylammonium chloride (10 mole%) to an average molecular weight of about 8 million in the presence of a homopolymer of acryloyloxyethyltrimethylammonium chloride having a molecular weight of about 10,000; deionized water; ammonium sulphate and a polymerization initiator. The resulting polymer mixture had a weight ratio HMW polymer to LMW polymer of 2.7:1, and a dry polymer content of about 18.5%. The polymer mixture was diluted to a dry polymer content of 0.1% prior to use.

[0033] Polymers used for comparison purposes were: P1) a HMW cationic polyacrylamide having a molecular weight of about 8 million; and P2) a HMW cationic polyacrylamide having a molecular weight of about 16 million. The polymers P1 and P2 were dissolved in water and used as 0.1% aqueous solutions.

[0034] The anionic inorganic material used was a silica based sol of the type disclosed in US-A-5,368,833. The sol had an S-value of about 25% and contained silica particles with a specific surface area of about 900 m<sup>2</sup>/g which were surface-modified with aluminium to a degree of 5%. This sol is designated Sol 1. Sol 1 was added in an amount of 0.8 kg/ton, calculated as dry particles on dry stock system.

[0035] Table 1 shows the drainage time at varying dosages of P1, P2 and M1, calculated as dry polymer on dry stock system.

Table 1

Polymer used	Drainage time [seconds] at polymer dosage of			
	0.5 kg/ton	0.8 kg/ton	1.2 kg/ton	2.0 kg/ton
P1	15.7	15.4	11.4	6.3
P2	15.7	14.0	11.8	6.6
M1	14.9	13.0	7.5	4.8

[0036] As can be seen from Table 1, the process using the mixture of LMW and HMW cationic polymers according to the invention resulted in improved drainage.

#### Example 2

[0037] In this test series, retention was evaluated by means of the DDA used in Example 1 in combination with a nephelometer. First pass retention was evaluated by measuring the turbidity of the filtrate, the white water, obtained by draining the stock. The polymers and anionic inorganic particles according to Example 1 were similarly used in this test series.

[0038] Table 2 shows the retention effect measured as turbidity of white water obtained at varying dosages of P1, P2 and M1, calculated as dry polymer on dry stock system.

Table 2

Polymer used	Turbidity [NTU] at polymer dosage of			
	0.5 kg/ton	0.8 kg/ton	1.2 kg/ton	2.0 kg/ton
P1	236	149	87	42
P2	246	165	100	40
M1	161	90	53	29

[0039] As can be seen from Table 2, the process according to the invention using a mixture of HMW and LMW cationic polymers resulted in markedly improved first pass retention.

#### Example 3

[0040] Retention was evaluated as in Example 2, except that different polymers were used. The order of addition according to Example 1 was applied, unless otherwise indicated.

[0041] A polymer mixture designated M2 was prepared by dissolving the HMW cationic polyacrylamide P2 according to Example 1 in an aqueous solution of a LMW cationic polyamine having a molecular weight of 50,000, which is designated P3. M2 had a weight ratio P2 to P3 of 2.7:1.

[0042] Another embodiment of the invention was tested in which use was made of a freshly prepared mixture of P2 and P3. An aqueous solution of P2 was brought into contact with an aqueous solution of P3 by means of a mixing device, where the separate solutions were intimately mixed for about 2-3 seconds prior to introducing the resulting solution into the stock. The polymers were added in a weight ratio P2 to P3 of 2.7:1. This mixture is designated M3.

[0043] A further embodiment of the invention, designated S1, was tested in which P2 and P3 were separately but simultaneously added to the stock in a weight ratio P2 to P3 of 2.7:1.

[0044] P2 and P3 were also used for comparison purposes, where P3 was added to the stock followed by stirring for 120 seconds before adding P2. The polymers were used in an amount corresponding to a weight ratio P2 to P3 of 2.7:1. In Table 3, this test is designated P3+P2. In one test, P2 was also used as a single cationic polymer additive.

[0045] Table 3 shows the retention effect observed when adding 1.2 kg of total polymer and 0.8 kg of silica based particles per ton of dry stock system. As can be seen from Table 3, considerably improved retention was obtained with the processes according to the present invention.

Table 3

	Total polymer addition, 1.2 kg/ton				
	P3+P2	P2	M2	M3	S1
Turbidity [NTU]	96	101	62	71	83

#### Example 4

[0046] First pass retention was evaluated as in Example 3, except that other types of additives were used. The furnish was based on 80% of a 80:20 mixture of peroxide bleached thermomechanical pulp:stoneground wood pulp and 20% of the pulp according to Example 1. To the stock obtained were added 30% of china clay, based on dry substance, 4 g/l of sodium acetate trihydrate and 10 mg/l of extractives. Stock volume was 800 ml, consistency 0.15% and pH 5.5.

[0047] Polymer mixtures designated M4 and M5 were prepared by dissolving HMW cationic polyacrylamide P1 according to Example 1 in aqueous solutions of LMW polymers. The LMW polymer used in M4 was a cationic polyacrylamide having a molecular weight of about 100,000 and a cationic charge density of 2.9 meq/g, which is designated P4. M4 had a weight ratio P4 to P1 of 1:1. The LMW polymer used in M5 was a cationic starch having a molecular weight of about 400,000 and a cationic charge density of 2.5 meq/g, which is designated P5. M5 had a weight ratio P5 to P1 of 1:1.

[0048] The polymer mixtures were compared to prior art processes in which the polymers P1, P4 and P5 were separately added and where the LMW polymers were added to the stock followed by stirring for 30 seconds before adding P1. The weight ratios of P4:P1 and P5:P1 were both 1:1. These comparison tests are designated P4+P1 and P5+P1.

[0049] The anionic inorganic particulate materials used were Sol 1 according to Example 1 and a silica sol of the type disclosed in US 4,388,150 which contained silica particles with a specific surface area of 500 m<sup>2</sup>/g, which is

# EP 0 752 496 B1

designated Sol 2. The amount of Sol 1 and Sol 2 added was 3.0 and 6.0 kg/ton, respectively, calculated as dry particles on dry stock system.

[0050] Table 4 shows the retention effect, measured as turbidity, when using varying amounts of polymer, calculated as dry polymer on dry stock system, in combination with the sols.

Table 4

Polymer used	Sol used	Turbidity [NTU] at polymer dosage [kg/ton]						
		1.0	2.0	3.0	4.0	6.0	8.0	10.0
P4+P1	Sol 1	100	72	50	44	-	16	-
M4	Sol 1	80	59	45	40	-	8	-
P4+P1	Sol 2	-	-	-	-	37	30	32
M4	Sol 2	-	-	-	-	27	17	13
P5+P1	Sol 1	-	62	-	42	-	13	13
M5	Sol 1	-	61	-	38	-	9	4

## Example 5

[0051] The procedure of Example 4 was followed except that different polymers were used. Cationic potato starch designated P6 was used as the HMW polymer and the polyamine P3 according to Example 3 was used as the LMW polymer. A polymer mixture designated M6 was obtained by mixing the polymers in the form of aqueous solutions in a weight ratio P6 to P3 of 5:1.

[0052] Table 4 shows the retention effect obtained with varying amounts of P3+P6 and M6, calculated as dry polymer on dry stock system, when the polymers were used in combination with Sol 1 added in an amount of 3.0 kg/ton.

Table 5

Polymer used	Turbidity [NTU] at polymer dosage of	
	18 kg/ton	24 kg/ton
P3+P6	28	27
M6	20	18

## Example 6

[0053] Further cationic polymers and anionic inorganic particles were evaluated for retention performance by means of a Britt Dynamic Drainage Jar at a stirring speed of 1000 rpm, which is conventional in the art. The stock and polymers used in Example 4 were similarly used in this test series. The anionic inorganic particles used were a suspension of the type disclosed in WO-A-94/05595 containing silica based particles according to Example 1 and natural sodium bentonite in a weight ratio of 2:1, designated Susp 1, and a suspension of natural sodium bentonite, designated Susp 2. The amount of Susp 1 and Susp 2 added was 4.0 and 6.0 kg/ton, respectively, calculated as dry on dry stock system.

[0054] Table 6 set forth the first pass retention of fines and filler at varying polymer dosages, calculated as dry polymers on dry stock system.

Table 6

Polymer used	Suspension used	Retention [%] at polymer dosage [kg/ton]			
		1	2	4	5
P4+P1	Susp 1	26.1	32.2	56.7	70.5
M4	Susp 1	29.4	43.0	61.9	75.1
P4+P1	Susp 2	-	43.5	43.5	-
M4	Susp 2	-	46.5	61.6	-

## Claims

1. A process for the production of paper from a suspension of cellulose containing fibres, and optional fillers, wherein



- a low molecular weight cationic organic polymer, a high molecular weight cationic or amphoteric polymer and anionic inorganic particles are added to the suspension and the suspension is formed and drained on a wire, **characterised in that** the low molecular weight polymer has a molecular weight below 700,000, the high molecular weight polymer has a molecular weight above 1,000,000 and that said polymers are simultaneously added to the suspension with substantially no time difference and essentially at the same position.
2. A process according to claim 1, **characterised in that** the low molecular weight polymer and the high molecular weight polymer are added to the suspension in the form of a mixture.
  3. A process according to claim 1, **characterised in that** the low molecular weight polymer and the high molecular weight polymer are simultaneously but separately added to the suspension.
  4. A process according to claim 1, 2 or 3, **characterised in that** the high molecular weight polymer is cationic starch, cationic guar gum or cationic acrylamide-based polymer.
  5. A process according to claim 1, 2 or 3, **characterised in that** the low molecular weight cationic polymer is modified starch, polyamine, polyethylene imine, polyamideamine/epichlorohydrin, dimethylamine/epichlorohydrin or a homo- or copolymer based on monomers selected from diallyldimethyl ammonium chloride, vinylamines, (meth)acrylamides, (meth)acrylates, or mixtures thereof.
  6. A process according to any of the preceding claims, **characterised in that** the weight ratio of high molecular weight polymer to low molecular weight polymer is within the range of from 9:1 to 1:3.
  7. A process according to any of the preceding claims, **characterised in that** the low molecular weight polymer has a higher cationicity and/or higher cationic charge density than the high molecular weight polymer.
  8. A process according to any of the preceding claims, **characterised in that** the anionic inorganic particles are silica based particles.
  9. A process according to claim 8, **characterised in that** the silica based particles are colloidal silica, colloidal aluminium modified silica, colloidal aluminium silicate or polysilicic acid.
  10. A process according to any of claims 1 to 7, **characterised in that** the anionic inorganic particles are bentonite.
  11. A polymer mixture in the form of an aqueous dispersion, **characterised in that** it comprises at least one high molecular weight cationic or amphoteric acrylamide-based polymer having a molecular weight above 1,000,000, at least one low molecular weight cationic organic polymer having a molecular weight below 700,000 and at least one water-soluble inorganic salt, wherein the weight ratio of said high molecular weight polymer to said low molecular weight polymer is within the range of from 9:1 to 1:2 and the dispersion comprises particles of high molecular weight cationic or amphoteric acrylamide-based polymer.
  12. A polymer mixture according to claim 11, **characterised in that** the high molecular weight acrylamide-based polymer is cationic and that the low molecular weight cationic polymer is a homo- or copolymer based on monomers selected from diallyldimethyl ammonium chloride, (meth)acrylamides, (meth)acrylates, or mixtures thereof.
  13. A polymer mixture according to claim 11 or 12, **characterised in that** the dry polymer content is ranging from 10 to 60% by weight.
  14. A polymer mixture according to claim 11, 12 or 13, **characterised in that** the inorganic salt is sodium sulfate, ammonium sulfate, magnesium sulfate or aluminium sulfate and that the inorganic salt is present in an amount of at least 5% by weight, based on the dispersion.

#### Patentansprüche

1. Verfahren zur Herstellung von Papier aus einer Cellulosesuspension, die Fasern und gegebenenfalls Füllstoffe enthält, wobei der Suspension ein niedermolekulares kationisches organisches Polymer, ein hochmolekulares kationisches oder amphoterisches Polymer und anionische anorganische Teilchen zugegeben werden und die Sus-

pension gebildet wird und auf einem Draht abtropfen gelassen wird, **dadurch gekennzeichnet, daß** das niedermolekulare Polymer ein Molekulargewicht unter 700.000 aufweist, das hochmolekulare Polymer ein Molekulargewicht über 1.000.000 aufweist, und daß die Polymere der Suspension gleichzeitig im wesentlichen ohne Zeitunterschied und im wesentlichen an der gleichen Stelle zugegeben werden.

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2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, daß** das niedermolekulare Polymer und das hochmolekulare Polymer der Suspension in Form eines Gemischs zugegeben werden.

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3. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, daß** das niedermolekulare Polymer und das hochmolekulare Polymer der Suspension gleichzeitig, jedoch getrennt zugegeben werden.

4. Verfahren nach Anspruch 1, 2 oder 3, **dadurch gekennzeichnet, daß** das hochmolekulare Polymer kationische Stärke, kationisches Guarmehl oder kationisches Polymer auf Acrylamid-Basis ist.

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5. Verfahren nach Anspruch 1, 2 oder 3, **dadurch gekennzeichnet, daß** das niedermolekulare kationische Polymer modifizierte Stärke, Polyamin, Polyethylenimin, Polyamidamin/Epichlorhydrin, Dimethylamin/Epichlorhydrin, oder ein Homo- oder Copolymer auf der Basis von Monomeren ist, die aus Diallyldimethylammoniumchlorid, Vinylaminen, (Meth)acrylamiden, (Meth)acrylaten oder Gemischen davon ausgewählt sind.

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6. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, daß** das Gewichtsverhältnis von hochmolekularem Polymer zu niedermolekularem Polymer im Bereich von 9:1 bis 1:3 liegt.

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7. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, daß** das niedermolekulare Polymer eine höhere Kationizität und/oder höhere kationische Ladungsdichte als das hochmolekulare Polymer aufweist.

8. Verfahren nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet, daß** die anionischen anorganischen Teilchen auf Kieselsäure-Basis sind.

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9. Verfahren nach Anspruch 8, **dadurch gekennzeichnet, daß** die Teilchen auf Kieselsäure-Basis kolloidale Kieselsäure, kolloidale Aluminium-modifizierte Kieselsäure, kolloidales Aluminiumsilicat oder Polykieselsäure sind.

10. Verfahren nach einem der Ansprüche 1 bis 7, **dadurch gekennzeichnet, daß** die anionischen anorganischen Teilchen Bentonit sind.

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11. Polymergemisch in Form einer wäßrigen Dispersion, **dadurch gekennzeichnet, daß** sie mindestens ein hochmolekulares kationisches oder amphoterisches Polymer auf Acrylamid-Basis mit einem Molekulargewicht über 1.000.000, mindestens ein niedermolekulares kationisches organisches Polymer mit einem Molekulargewicht unter 700.000 und mindestens ein wasserlösliches anorganisches Salz umfaßt, wobei das Gewichtsverhältnis des hochmolekularen Polymers zu dem niedermolekularen Polymer im Bereich von 9:1 bis 1:2 liegt und die Dispersion Teilchen aus hochmolekularem kationischem oder amphoterischem Polymer auf Acrylamid-Basis umfaßt.

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12. Polymergemisch nach Anspruch 11, **dadurch gekennzeichnet, daß** das hochmolekulare Polymer auf Acrylamid-Basis kationisch ist, und daß das niedermolekulare kationische Polymer ein Homo- oder Copolymer auf der Basis von Monomeren ist, die aus Diallyldimethylammoniumchlorid, (Meth)acrylamiden, (Meth)acrylaten oder Gemischen davon ausgewählt sind.

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13. Polymergemisch nach Anspruch 11 oder 12, **dadurch gekennzeichnet, daß** der Polymer-Trockengehalt im Bereich von 10 bis 60 Gew.-% liegt.

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14. Polymergemisch nach Anspruch 11, 12 oder 13, **dadurch gekennzeichnet, daß** das anorganische Salz Natriumsulfat, Ammoniumsulfat, Magnesiumsulfat oder Aluminiumsulfat ist, und daß das anorganische Salz in einer Menge von mindestens 5 Gew.-%, bezogen auf die Dispersion, vorhanden ist.

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## Revendications

1. Procédé pour produire du papier à partir d'une suspension de fibres contenant de la cellulose, et des charges

- éventuelles, dans lequel on ajoute à une suspension un polymère organique cationique de faible masse moléculaire, un polymère amphotère ou cationique, de masse moléculaire élevée et des particules inorganiques anioniques, et la suspension est formée et égouttée sur une toile métallique, **caractérisé en ce que** le polymère de faible masse moléculaire présente une masse moléculaire inférieure à 700 000, le polymère de masse moléculaire élevée présente une masse moléculaire supérieure à 1 000 000, et **en ce que** lesdits polymères sont simultanément ajoutés à la suspension, sensiblement en même temps et essentiellement au même endroit.
2. Procédé selon la revendication 1, **caractérisé en ce que** le polymère de faible masse moléculaire et le polymère de masse moléculaire élevée sont ajoutés à la suspension sous la forme d'un mélange.
  3. Procédé selon la revendication 1, **caractérisé en ce que** le polymère de faible masse moléculaire et le polymère de masse moléculaire élevée sont ajoutés simultanément mais séparément à la suspension.
  4. Procédé selon la revendication 1, 2 ou 3, **caractérisé en ce que** le polymère de masse moléculaire élevée est un amidon cationique, une gomme de guar cationique ou un polymère cationique à base d'acrylamide.
  5. Procédé selon la revendication 1, 2 ou 3, **caractérisé en ce que** le polymère cationique de faible masse moléculaire est un amidon modifié, une polyamine, un polyéthylène-imine, un polyamidoamine/épichlorhydrine, une diméthylamine/épichlorhydrine ou un homopolymère ou copolymère à base de monomères choisis parmi les chlorures de diallyldiméthylammonium, les vinylamines, les (méth)acrylamides, les (méth)acrylates et leurs mélanges.
  6. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** le rapport pondéral du polymère de masse moléculaire élevée au polymère de faible masse moléculaire se situe dans l'intervalle allant de 9:1 à 1:3.
  7. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** le polymère de faible masse moléculaire présente un caractère cationique supérieur ou une densité de charge cationique supérieure à ceux du polymère de masse moléculaire élevée.
  8. Procédé selon l'une quelconque des revendications précédentes, **caractérisé en ce que** les particules inorganiques anioniques sont des particules à base de silice.
  9. Procédé selon la revendication 8, **caractérisé en ce que** les particules à base de silice sont de la silice colloïdale, de la silice colloïdale modifiée par de l'aluminium, du silicate d'aluminium colloïdal ou de l'acide polysilicique.
  10. Procédé selon l'une quelconque des revendications 1 à 7, **caractérisé en ce que** les particules inorganiques anioniques sont la bentonite.
  11. Mélange de polymères sous la forme d'une dispersion aqueuse, **caractérisé en ce qu'il** comprend au moins un polymère cationique ou amphotère, à base d'acrylamide, de masse moléculaire élevée présentant une masse moléculaire supérieure à 1 000 000, au moins un polymère organique cationique de faible masse moléculaire présentant une masse moléculaire inférieure à 700 000, et au moins un sel inorganique soluble dans l'eau, dans lequel le rapport pondéral entre ledit polymère de masse moléculaire élevée et ledit polymère de faible masse moléculaire se situe dans l'intervalle allant de 9:1 à 1:2, et la dispersion comprend des particules de polymère cationique ou amphotère, à base d'acrylamide, de masse moléculaire élevée.
  12. Mélange de polymères selon la revendication 11, **caractérisé en ce que** le polymère à base d'acrylamide, de masse moléculaire élevée est cationique, et **en ce que** le polymère cationique de faible masse moléculaire est un homopolymère ou un copolymère à base de monomères choisis parmi les chlorures de diallyldiméthylammonium, les (méth)acrylamides, les (méth)acrylates, et leurs mélanges.
  13. Mélange de polymères selon la revendication 11 ou 12, **caractérisé en ce que** la teneur en polymères secs se situe dans l'intervalle allant de 10 à 60 % en poids.
  14. Mélange de polymères selon la revendication 11, 12 ou 13, **caractérisé en ce que** le sel inorganique est le sulfate de sodium, le sulfate d'ammonium, le sulfate de magnésium ou le sulfate d'aluminium et **en ce que** le sel inorganique est présent en une quantité d'au moins 5 % en poids par rapport à la dispersion.

